

Optimization on Temperatures of Filament and Substrate for High-Quality Narrow Gap $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$ Alloys Grown by Hot-Wire CVD

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Optimization of Filament and Substrate Temperatures for High-Quality Narrow-Gap a-Si_{1-x}Ge_x:H Alloys Grown by Hot-Wire CVD

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ABSTRACT

We improve narrow-bandgap ($1.2 < E_{\text{Tauc}} < 1.3$ eV) amorphous silicon germanium (a-Si_{1-x}Ge_x:H) alloys grown by hot-wire chemical vapor deposition (HWCVD) by lowering both substrate and filament temperatures. We grew two series of films using a tungsten filament. First we systematically varied the filament temperature (T_f) from our standard temperature of 2150°C down to 1750°C, while fixing all other deposition parameters. Secondly we systematically varied the substrate temperature (T_s) from our previous optimized temperature of 350°C down to 125°C, while fixing all other deposition parameters including $T_f = 1800^\circ\text{C}$. Films with the best properties are grown with $T_f < 1880^\circ\text{C}$ and T_s between 200°-250°C. Improvement of the material properties are characterized by improvements in the H-bonding, reduced microvoid density, and good photoresponse (for a given E_{Tauc}). There are about 15% more Ge-H bonds—passivating Ge-dangling bonds—relative to our previous work. The films are more compact due to microvoid reduction as measured by small-angle X-ray scattering (SAXS). We also fabricated solar cells with these optimized materials and obtained ~3.58%-efficient devices without doing bandgap profiling yet. Due to the high optical absorption of these a-Si_{1-x}Ge_x:H (~1.25 eV bandgap) alloys, we need an i-layer that is only ~1200 Å thick to obtain a J_{sc} of ~20 mA/cm². Additionally, we increased the GeH₄ gas utilization relative to SiH₄ from previous work, which was about 1:1 (GeH₄ in gas to Ge in film). Under the current conditions, a 35% GeH₄ gas fraction produces an a-Si_{1-x}Ge_x:H film with $x = 0.7$.

Introduction

It is well known that a-Si_{1-x}Ge_x:H alloys are essential for the fabrication of multijunction solar cells. The world-record cell (14.6% initial efficiency) was made by USSC using these alloys as the middle and bottom cells [1]. Our early attempts to grow “device quality” a-Si_{1-x}Ge_x:H with bandgaps below 1.5 eV by HWCVD had limited success [2]. Those films were grown under conditions that give “device quality” a-Si:H, namely, high T_f and T_s . By decreasing both T_f and T_s , as well as reducing our filament diameter from 0.5 mm to 0.38 mm, we now grow films with optoelectronic properties equal to films grown by PE CVD [3].

Experiment

All the samples used in this paper are grown in a HWCVD tube reactor [3]. The main deposition parameters for the two series grown for this study are in Table 1.

Table 1: Summary of Main Deposition Parameters

| Sample (Set 1) | T_f (°C) | T_s (start) (°C) | Thick. (Å) | R_d (Å/s) |
|----------------|------------|--------------------|------------|-------------|
| L902 | 2150 | 180 | 2976 | 9.92 |
| L904 | 2065 | 180 | 3434 | 8.18 |
| L905 | 1975 | 180 | 3315 | 6.50 |
| L907 | 1880 | 180 | 2997 | 4.16 |
| L911 | 1800 | 180 | 2128 | 2.03 |
| L913 | 1750 | 180 | 2085 | 0.98 |
| L908 | 1800 | 350 | 2919 | 3.04 |
| L894 | 1800 | 300 | 4087 | 3.45 |
| L895 | 1800 | 250 | 3669 | 3.08 |
| L896 | 1800 | 200 | 3622 | 2.92 |
| L897 | 1800 | 150 | 3501 | 2.84 |
| L898 | 1800 | 125 | 2856 | 2.14 |

We deposited each sample simultaneously on a 2.5-cm x 2.5-cm 1737F Corning glass substrate and a 2.5-cm x 1.5-cm c-Si wafer. We evaporated coplanar (width to length = 0.05) Cr contacts on the films on the 1737F substrates for conductivity measurements using a Keithley model 6517a electrometer. The photoconductivity is measured under an ELH lamp set to approximate an AM1.5 solar spectrum. We perform UV/Visible optical spectroscopy using an n&k 1280 analyzer on the films grown on 1737F substrates to determine the thickness, bandgap, refractive index (n), and the extinction coefficient (k). Note that this instrument readily calculates an E_{04} gap, that is, the photon energy where the optical absorption is 10^4 . The Tauc bandgap is taken from the fitting of E vs. $(\alpha h\nu)^{1/2}$, in which α is calculated by the method of interference-free determination of optical absorption coefficient on the raw data of transmission and reflectance from this spectrometer [4]. We use the films deposited on the c-Si for two structural measurements. We use Fourier transform infrared spectroscopy (FTIR) to calculate the hydrogen content (C_H), and study the hydrogen-bonding configuration to Si and Ge. We use secondary-ion mass spectroscopy (SIMS) to determine the Ge solid fraction (x) in the films.

For SAXS measurements, we duplicate the growth conditions from Table 1 in separate runs and deposit on high-purity aluminum foil. The total integrated SAXS intensity, Q_T , is a good measure of the overall film heterogeneity. The SAXS technique and analysis methods are described elsewhere [5].

Results and Discussion

1. FTIR Results

In Fig. 1, we display the FTIR spectra between 1700 and 2200 cm^{-1} , along with the superpositions of Gaussian fits to these spectra, for both film series. The absorption peaks for Ge-H, Ge-H₂, Si-H, and Si-H₂ bonding configurations are 1880, 1980, 2000, and 2090 cm^{-1} , respectively [6]. Because dihydride bonding (Ge-H₂ and Si-H₂) is deleterious to film quality, the best films are grown with $T_f < 1880^\circ\text{C}$ and T_s between 200-250°C. This assertion is consistent with photoconductivity and photoresponse data to be presented with additional analysis at the upcoming MRS meeting [7].

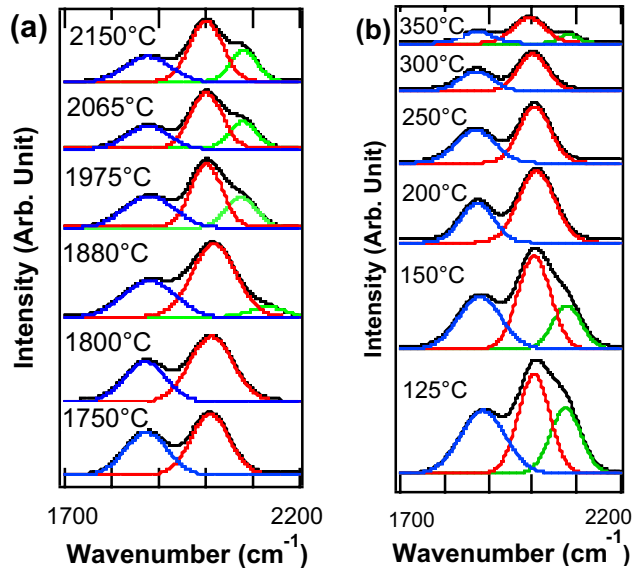


Figure 1: FTIR bonding configurations for the T_f series (a) and the T_s series (b).

2. SAXS and SIMS Results

In Fig. 2, we display both the total integrated SAXS intensity (Q_T) and the x as measured by SIMS, for both film series. There is a monotonic decrease in film heterogeneity (probably a decrease in microvoid density) as well as an increase in the germanium content of the films as the filament temperature is lowered from 2150° to 1750°C (Fig. 2a). There is a clear minimum in Q_T for the T_s series, centered at 220°C, whereas there is a decrease in x for increasing T_s . This minimum in Q_T correlates with the minimum in the dihydride bonding in the films, supporting the interpretation that -H₂ bonding occurs on void surfaces; as the heterogeneity increases, the -H₂ bonding increases.

Conclusions

We improved narrow-gap ($1.2 < E_g < 1.3$ eV) a-Si_{1-x}Ge_x:H alloys by optimizing T_f and T_s to reduce the dihydride bonding in the films and thus improve their optoelectronic properties. These materials are device quality, and further work is necessary to implement them in bandgap-graded device structures. Additionally, we will quantify the effect of deposition rate on film quality due to process changes.

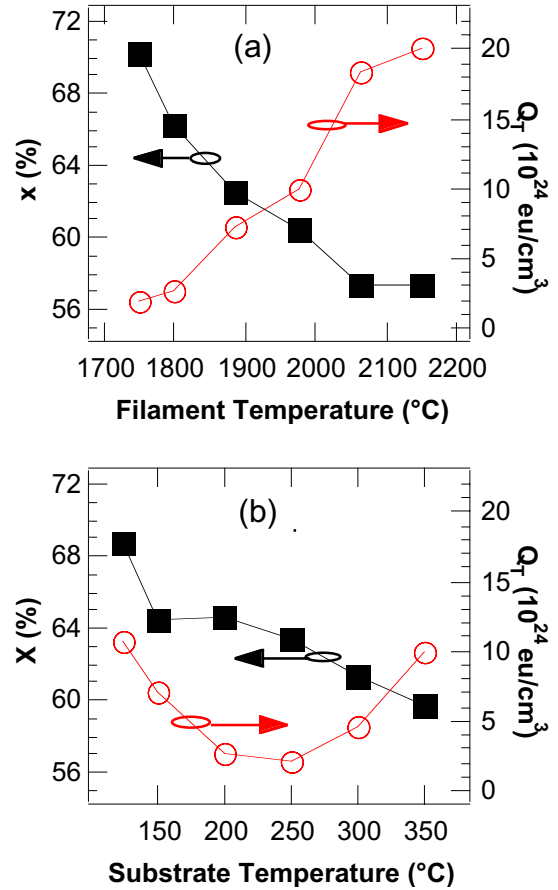


Figure 2: Ge fraction in the film by SIMS (x , left axis) and total integrated SAXS intensity (Q_T , right axis) for the T_f series (a) and the T_s series (b).

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References

- [1] J. Yang, A. Banerjee, and S. Guha, Appl. Phys. Lett. 70 (1997) 2975
- [2] B.P. Nelson, Y. Xu, D.L. Williamson, B. von Roedern, A. Mason, S. Heck, A.H. Mahan, S.E. Schmitt, A.C. Gallagher, J. Webb, and R. Reedy, Mat. Res. Soc. Symp., Proc. 507 (1998) p. 447
- [3] Y. Xu, B.P. Nelson, L.M. Gedvilas, and R.C. Reedy, September 2002, 2nd International Conference on Cat-CVD (Hot-Wire CVD) Process, Denver, CO, submitted to Thin Solid Films
- [4] Y. Hishikawa, et al., Japan. Jour. of App. Phys. Vol. 30, No. 5, May (1991) pp. 1008-1014
- [5] D.L. Williamson, Mat. Res. Soc. Symp. Proc. Vol. 377 (1995) p. 251
- [6] M. K. Bhan, L.K. Malhotra, and S. C. Kashyap, Jour. Appl. Phys. 66(6), 15 September 1989, pp. 2528-2537
- [7] Y. Xu, et al., to be published in the 2003 Mat. Res. Soc. Symp. Proc., Symposium A

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